

# SOLUTE TRANSPORT AS AN INDICATOR OF MORPHODYNAMIC ZONATION IN A POSTGLACIAL ENVIRONMENT, WEST POMERANIA, POLAND

MAŁGORZATA MAZUREK\*

*Quaternary Research Institute, Adam Mickiewicz University, ul. Fredry 10, Poznań, Poland*

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## ABSTRACT

Variations in the chemistry of dissolved sediment transported fluvially reflect the dynamics of soil leaching and erosion in the catchment. In this study, spatial changes in the concentrations of selected chemical parameters of surface waters have been used as natural geochemical indicators of variability in the chemical denudation processes operating in a postglacial catchment with a temperate climate. Hydrochemical mapping, supplemented by hydrological mapping, has been used to analyse the sources and hydrological pathways of solutes in the catchment. The field research was conducted in a small catchment drained by the Kluda River, Poland. This is a part of the upper Parseta hydrographic system, which is considered to be representative of the postglacial lakeland zone of West Pomerania and the Polish Plain. The study is based on hydrological and hydrochemical data from the period 1990–1993. Variations in the physical and chemical parameters of those waters reveal considerable differences in surface water properties in the catchment. A grouping procedure and principal components analysis carried out on the basis of 10 physico-chemical parameters characterizing the measurement sites produced four hydrochemical groups. The results emphasize that the physico-chemical properties of the surface water depend not only on spatial variability in catchment lithology, soils, land use and topography, but also the contact time and pathways by which water reaches the drainage network. Hydrological pathways in the slope system and their importance to the supply of solutes to the channel system provided a basis for distinguishing four morphodynamic zones (divide, plateau, escarpment and valley) in the Kluda catchment. The contributions of water and solutes to the river channel from these morphodynamic zones are distinctly different. Copyright © 1999 John Wiley & Sons, Ltd.

KEY WORDS: solute transport; geochemical indicators; catchment variability; postglacial environments; Polish Plain

## INTRODUCTION

Fluvial transport is one of the dominant processes of the contemporary denudation system of the temperate zone and is a good indicator of the erosion and soil leaching processes which operate in a catchment system. Studies of the concentrations of dissolved and suspended material have been carried out for decades in various catchments around the world (Gregory and Walling, 1973; Milliman *et al.*, 1995; Walling and Webb, 1983, 1986). These studies have demonstrated that the solute load usually constitutes a substantial proportion of the total load of sediment in temperate climates. The proportion of the total load transported in solution by rivers draining the postglacial zone of the Polish Plain, including rivers in the lakeland zone of Pomerania, has been documented through observation. For example, Cyberski (1984) estimated the total load in the lakeland catchments to be  $45$  to  $78 \text{ t km}^{-2} \text{ a}^{-1}$ , of which dissolved material made up 71 to 88 per cent. Similar figures were obtained by Golebiewski (1981), Kostrzewski *et al.* (1994), Kostrzewski and Zwoliński (1990, 1992a,b), Smolska (1996), Wilamski (1978) and Zwoliński (1989, 1993).

These findings can be compared with those obtained from research performed in areas of young moraine deposits in eastern Denmark by Hasholt (1983), who reports that the dissolved load varies there from 63 to

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\* Correspondence to: M. Mazurek, Quaternary Research Institute, Adam Mickiewicz University, ul. Fredry 10, Poznań, Poland.  
E-mail: gmazurek@amu.edu.pl

$148 \text{ t km}^{-2} \text{ a}^{-1}$ . He maintains that in order to obtain the load of dissolved sediment derived from weathering processes one has to subtract the solutes contributed by rain and throughflow, which amount to  $22 \text{ t km}^{-2} \text{ a}^{-1}$ . According to Mansikkaniemi (1982), the quantities of dissolved material transported from a basin close to the coast of southwestern Finland accounted for over 60 per cent of the total load. This proportion declined rapidly with distance up-river, although solutes still constituted 49 per cent of total load in the Paimionjoki drainage basin.

The main factor that controls the movement of dissolved material in a catchment and its supply to the river channels is the nature of runoff pathways. The various pathways by which water reaches a river channel, together with the availability of dissolved substances, are of fundamental significance for the timing, magnitude and transport dynamics of material supplied from the catchment to the river channel. Thus, from the geomorphological point of view, it is fundamentally important to identify the zones supplying runoff and the pathways by which that water reaches a river channel in order to identify the corresponding sources of supply of dissolved load.

In practice it is difficult to judge the spatial diversity of the sources supplying these substances to river channels on the basis of at-a-station measurements. Consequently, analysis of processes responsible for the supply of the dissolved load to a river channel, performed together with a spatial analysis of the supply zones, provides the only basis for determining the denudational activity of the fluvial system that drives the contemporary development of catchment relief (Finlayson, 1977; Froehlich, 1992).

Much of the land area of the northern hemisphere is covered by glacial and glaciofluvial deposits. The texture, mineralogy and petrology of these deposits are, in general, highly variable, both regionally and stratigraphically. While this complicates attempts to establish regional denudation rates, it provides the opportunity to use variations in solute chemistry to analyse supply processes and identify source zones.

In the case of the North Polish Lakeland, contrasts in geological structure, vertical and horizontal variability in the physico-chemical properties of the soils and sediment deposits, the presence of a variety of runoff pathways, and the development and organization of the river network all indicate considerable differences in the processes of contemporary fluvio-chemical denudation processes. Under natural conditions, solute yields in the North Polish Lakeland are determined by:

- (1) vertical and horizontal variations in soil texture as well as the distribution of glacial, fluvioglacial and Holocene deposits;
- (2) the geochemical character of deposits, especially the high content of calcium carbonate in the fine fraction of postglacial and Holocene deposits;
- (3) the hydrological cycle which, according to Dynowska (1991), is characterized by an abundant and regular supply throughout the year, high surface and groundwater retention, and a predominance of groundwater runoff; and
- (4) a poorly developed drainage network (Drwal, 1982).

Recently, the character of fluvial transport of dissolved sediment has also been modified significantly by human activity (Borowiec and Zabłocki, 1988; Kostrzewski and Zwoliński, 1985; Wilamski and Śliwa, 1978).

Recognizing the complexity of the solute source and transport system, the aim of the study reported here was to gain an insight into the nature and dynamics of the flow of dissolved substances in this environmentally heterogeneous, postglacial region. Changes in the concentrations of selected chemical constituents of surface waters were used as natural geochemical indicators of the spatial variability of fluvio-chemical denudation. Hydrochemical mapping, supplemented by hydrological mapping, was used to support spatial and temporal analyses of the source zones and hydrological pathways of solutes.

#### STUDY AREA: THE KLUDA RIVER BASIN

The study basin selected was the catchment of the Kluda River situated in the central part of West Pomerania. This is a small fourth-order stream (according to the Horton–Strahler classification) in the upper part of the

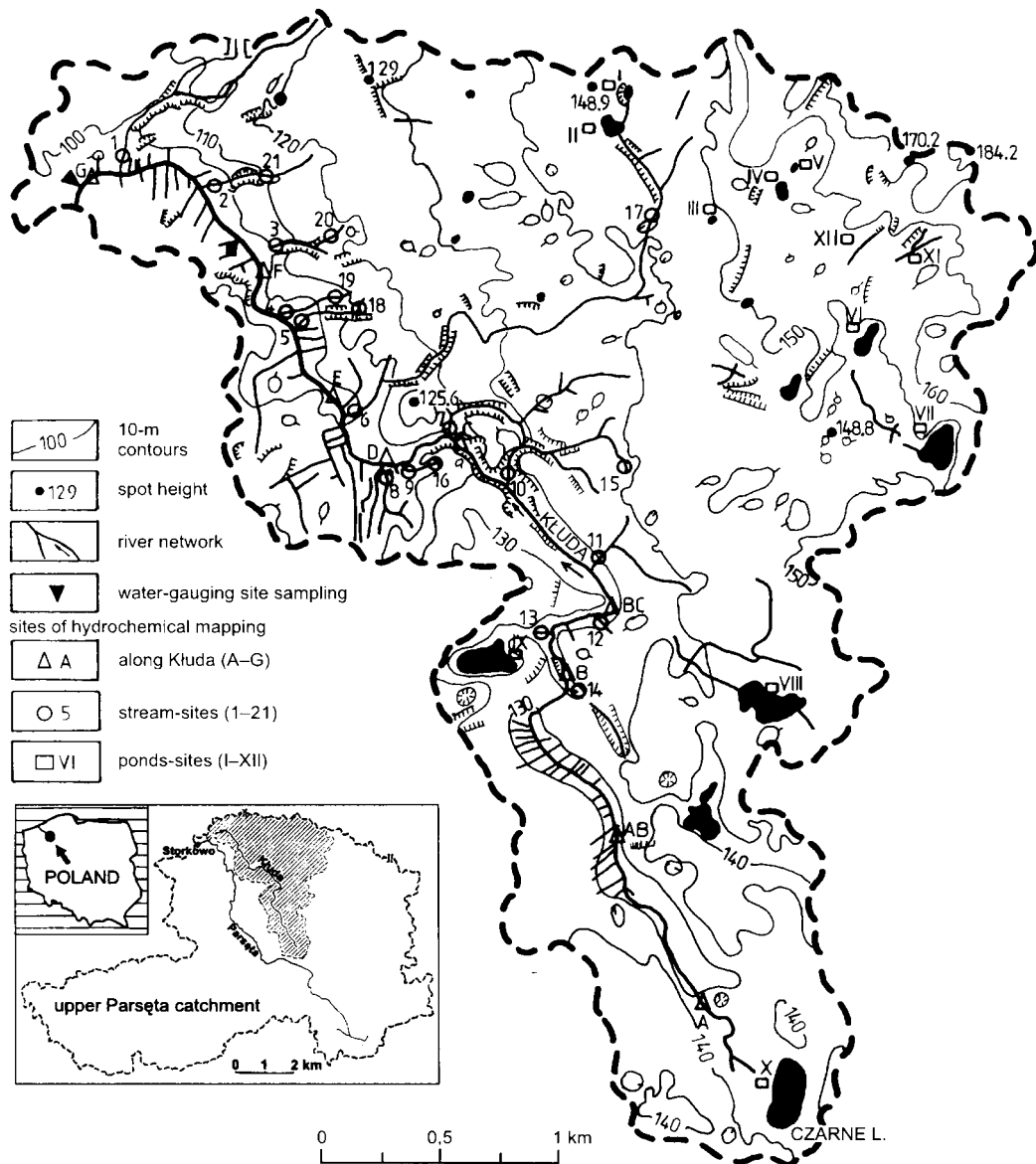


Figure 1. Location of the Kluda catchment (shaded) and measurement sites

Parsęta hydrological system. The catchment has an area of  $10.7 \text{ km}^2$  and a circumference of  $21.3 \text{ km}$ . The headwaters lie at an altitude of  $132 \text{ m a.s.l.}$ , and the river flows for about  $7 \text{ km}$  before it joins the Parsęta at  $88.7 \text{ m a.s.l.}$  (Figure 1).

## RESEARCH SCOPE AND METHODS

Field work was performed between 1 November 1989 and 31 October 1993. These were average years with respect to weather conditions and the operation of secular trends in fluvial processes. The annual precipitation was  $650 \text{ mm}$ , 11 per cent of which was snowfall. The mean annual air temperature was  $8^\circ\text{C}$ . The observation period was characterized by an even discharge regime, with the annual mean unit discharge of the Kluda of

$8.9 \text{ dm}^3 \text{ s}^{-1} \text{ km}^{-2}$ . The results obtained for this period can be regarded as representative of low and average discharges in the Kluda system.

There were 42 study sites, of which 12 were located on ponds, nine were distributed along the principal stream, the Kluda River, and 21 were located on tributaries (Figure 1). Study sites were selected to reflect the range of topographic, lithologic and land-use characteristics present in the catchment. Over the four-year study period, 41 hydrochemical measurements were made in the Kluda catchment. The small area of the catchment made it possible to study the chemistry of its waters under homogeneous hydrological conditions. Water samples were collected roughly every five weeks to assess long-term fluctuations in the spatial pattern of water chemistry. Because of the seasonal operation of a part of the stream network, the amount of water sampled during particular measurements depended on meteorological and hydrological conditions. In total, in excess of 1600 samples were collected.

At the stream sites, discharge measurements were made using the conductometric method (Finlayson, 1979; Østrem, 1964). In addition to water sampling and discharge measurements, the water pH was also measured. Laboratory analyses of filtered water samples included:

- (1) measurement of their specific electrical conductance (s.e.c.) (at a reference temperature of  $25^\circ\text{C}$ );
- (2) determination of the concentrations of calcium and chloride ions, calcium hardness and alkalinity by titration;
- (3) measurement of the concentrations of sodium and potassium ions by flame photometry;
- (4) spectrophotometric determination of the concentrations of sulphate and ionized silica; and
- (5) calculation of the magnesium ion content.

Hydrochemical analyses were conducted either at the Geocological Station at Storkowo or the Sedimentological Laboratory of the Quaternary Research Institute, Adam Mickiewicz University, Poznań.

## CONTROLS OF THE POSTGLACIAL DENUDATION SYSTEM

The Kluda catchment is typical of many basins in the region, having a postglacial geoecosystem with a temperate climate. The study area is located on the northern slope of the Middle Pomeranian end-moraine series within the so-called Parsęta lobe. Its relief is the result of deglaciation during the Pomeranian Phase of the Vistulian, and of the Late Glacial and Holocene morphogenetic cycle (Karczewski, 1985).

The Kluda catchment may be divided into two geomorphological zones. Part of the catchment lies in the outer sub-zone of dead-ice moraine and kame moraine (B in Figure 2) while the rest of it is located on part of the seventh morainic plateau level ( $D_1$  in Figure 2) on the north-facing slope of Pomerania (Karczewski, 1989).

The first zone, of kame-and-kettle (B, Figure 2), constitutes the eastern part of the catchment. It has a low-relief, hummocky terrain with elevations ranging between 185 and 130 m a.s.l. and gradients often exceeding  $8^\circ$ . Depositional landforms are composed of two lithofacies: a glacio-fluvial series and a moraine series. The characteristic morphological elements of the zone are kettle-holes, which have played a significant role in relief development through functioning as local denudation–accumulation centres.

The second geomorphological zone is situated within the morainic plateau ( $D_1$ , Figure 2) and lies at elevations between 130 and 89 m a.s.l. Local relief does not exceed 10 m, and while gradients are generally less than  $5^\circ$ , maximum values (still less than  $8^\circ$ ) are found in the plateau scarp zone. The undulating ground-moraine plain with small crevasse forms is formed in glaciofluvial deposits and sandy ablation tills in which 12–15 per cent of the material is finer than 0.002 mm (Karczewski, 1985).

Owing to the great variability of the occurrence and development of superficial deposits (Figure 2), the basin exhibits a number of soil types. Brown earths and podzolic soils (acid, brown-rusty and rusty-podzolic soils) have developed on loose and weakly loamy sands. These soils are characterized by a very acid or acid reaction, a low content of soluble salts, and the tendency to acidify the entire soil profile. This characteristic of these soils is due to their mechanical composition (a small proportion of clay) and mineralogical composition (the predominance of monocrystalline quartz with potassium feldspars, plagioclases and

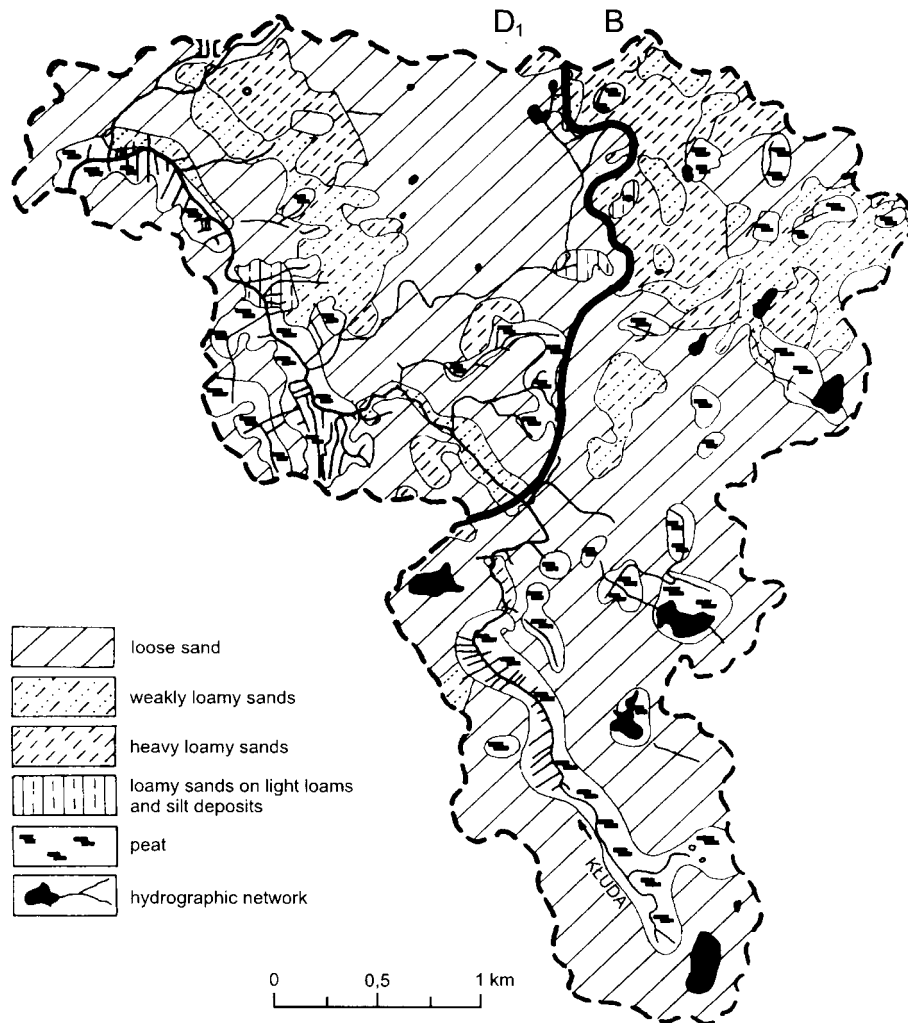


Figure 2. Lithology of the Kluda catchment. The boundary is marked between the outer sub-zone of dead-ice moraine and kame moraine (B), and the seventh morainic plateau level (D<sub>1</sub>)

muscovite). A small area (<15 per cent) of heavy loamy sands of medium permeability lying on light loams or silt deposits may be found. These soils have developed slightly acid leached brown soils and degraded black earths with higher contents of dissolved substances and organic matter. In the <2 mm fraction, clay minerals occur, mainly from the illite group, but also from the kaolinite and smectite groups, as well as a mixed illite–smectite group. The presence of these minerals and organic colloids determines the sorption and cation exchange capacities. Mud, peat and peat–mud soils from the Kluda valley have a slightly acid or neutral reaction and a high content of organic matter that gives them a large field moisture capacity and resistance to the action of acidifying factors.

The land-use mosaic in the Kluda catchment reflects the distribution of soils, lithology and landforms. As arable land and woodland occupy 71.8 per cent of the area, the Kluda catchment can be classified as predominantly agricultural woodland. Grassland is mostly found on the drained mineral-organic and organic soils that occur in kettle-holes and valleys. The basin is sparsely populated and there are no significant point sources of pollution.

The drainage network of the Kluda catchment is still in the process of development. Its major characteristic feature is the presence of a single, principal stream which flows along the entire length of the catchment and is

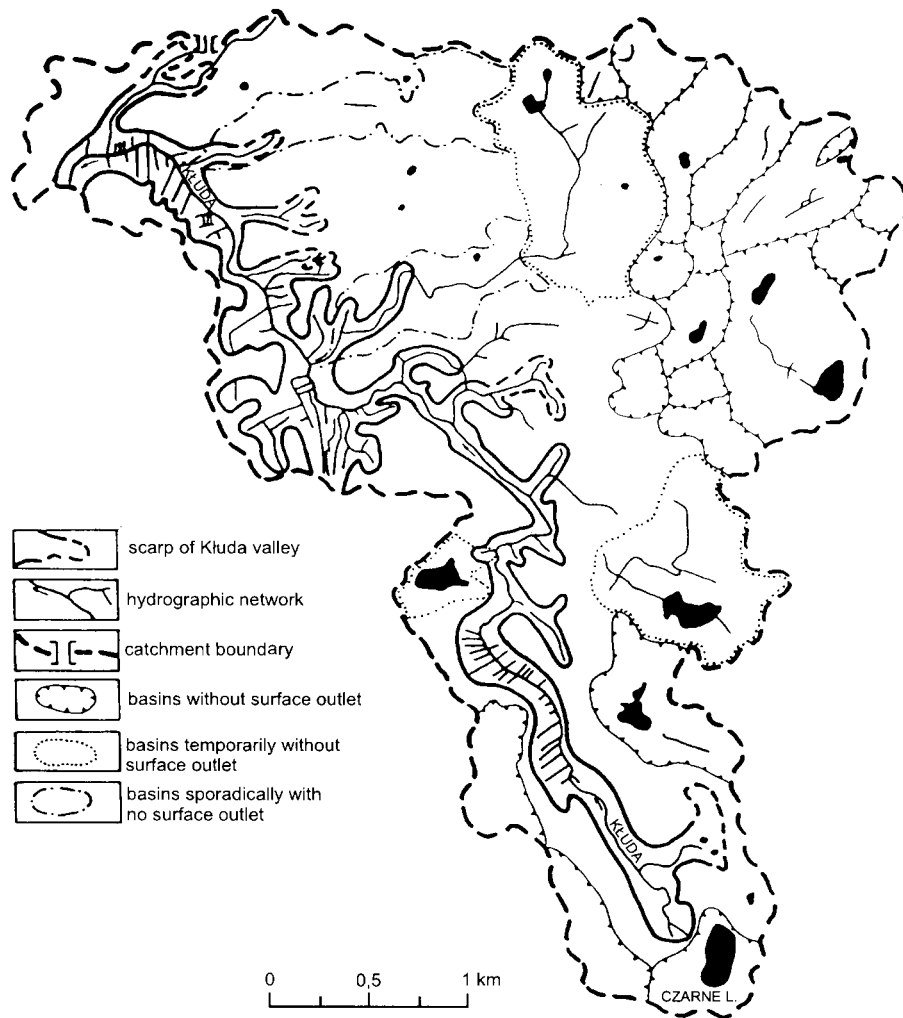


Figure 3. Surface water drainage system in the Kluda catchment

disproportionately long with respect to its tributaries (Figure 3). The mainstream is accompanied by a number of lower-order streams and ditches draining the valley floor. A characteristic of the valley of the Kluda River is the presence of reaches of different origins along its course. The valley may be classified as consisting of a series of wide melt-out basins connected by ravines. The lithological and morphological features of the valley and the channel in each reach reflect their contrasting origins.

Only 76.4 per cent of the Kluda catchment is actually drained by the surface drainage system. The remainder comprises the eastern and northeastern fragments of the catchment which have no surface water outlet (Figure 3). The lack of an outlet in these postglacial areas is due to local relief and geological structure.

These features of the Kluda catchment geosystem control the runoff and sediment yield of the basin and determine the character of transport in the fluvial system.

Table I. Variations of physico-chemical parameters of surface water in the Kluda catchment; from hydrochemical mapping in the hydrological years 1990–1993

Parameter	Range*	Parameter	Range*
Ca	1.6–92.0	SO <sub>4</sub>	0.9–91.2
Mg	0.1–13.9	PO <sub>4</sub>	0.0–9.8
Na	1.2–17.7	NO <sub>3</sub>	0.0–5.5
K	0.1–10.6	SiO <sub>2</sub>	0.1–18.6
HCO <sub>3</sub>	4.8–256.2	s.e.c. ( $\mu\text{S cm}^{-1}$ )	34–536
Cl	3.0–27.1	pH	5.04–9.84

\* Units are  $\text{mg dm}^{-3}$  except for s.e.c. and pH

### SURFACE WATER CHEMISTRY

Solute concentrations in surface waters of the Kluda catchment, expressed by specific conductance, vary in a wide range between 34 and 536  $\mu\text{S cm}^{-1}$ . There are equally wide variations in the physico-chemical parameters (Table I).

The stream water of the Kluda catchment belongs to the bicarbonate–calcium type, according to Monition's classification (Macioszczyk, 1987), which is characteristic of postglacial lakeland formed in deposits rich in calcium carbonate. These results are consistent with those derived from other studies of the chemistry of river water in West Pomerania (Gołębiewski, 1981 ; Kostrzewski *et al.*, 1993, 1994; Wilamski, 1978). In turn, the waters of the majority of ponds occurring in the catchment area can be classified as sulphate–calcium. The basic ionic components form the following sequences:

Streams	Other bodies of water
Ca > Mg > Na > K	Ca > Na > Mg > K
3.13 > 0.36 > 0.34 > 0.06 meq $\text{dm}^{-3}$	0.81 > 0.22 > 0.16 > 0.06 meq $\text{dm}^{-3}$
HCO <sub>3</sub> > SO <sub>4</sub> > Cl	SO <sub>4</sub> > HCO <sub>3</sub> > Cl
2.73 > 0.78 > 0.35 meq $\text{dm}^{-3}$	0.58 > 0.47 > 0.28 meq $\text{dm}^{-3}$

According to Caine and Thurman (1990), identification of the sources and flow paths of water and dissolved matter can be facilitated by principal components analysis of concentration data. The resultant diagram ordering the measuring sites in the Kluda catchment accounts for 61.5 per cent of the variance of the physico-chemical properties of water on the axis of the first component, and for 17.1 per cent of the variance on the axis of the second axis (Figure 4). The first two components are complementary and together account for 78.6 per cent of the total variance of nine parameters of the surface water of the Kluda catchment. It follows from the correlation matrix that the first component is identified with specific conductance ( $r = 0.98$ ), calcium cations ( $r = 0.96$ ), bicarbonate ions ( $r = 0.91$ ) and, to a lesser extent, with magnesium ions ( $r = 0.89$ ) and ionized silica ( $r = 0.88$ ). The variables having the highest correlations with the second component are potassium ( $r = 0.75$ ) and sulphate ions ( $r = 0.60$ ). The concentrations of sodium and chloride ions, in turn, do not contribute any significant information that could be used to better differentiate among the chemical composition groups of the Kluda catchment surface water.

The first principal component, PC1, may be identified with a groundwater source and interpreted as reflecting the share of constituents coming from the leaching of sub-soil deposits rich in calcium carbonate. Its higher value is due to the supply of water from more deep-seated aquifers, which takes longer to travel through the catchment.

The second principal component, PC2, characterizes the contents of potassium and sulphate ions whose main natural sources are mineral–organic and biologically active soil horizons and areas of organic accumulation. High values of these compounds are associated with the supply of water from shallow-seated sub-surface water bodies.

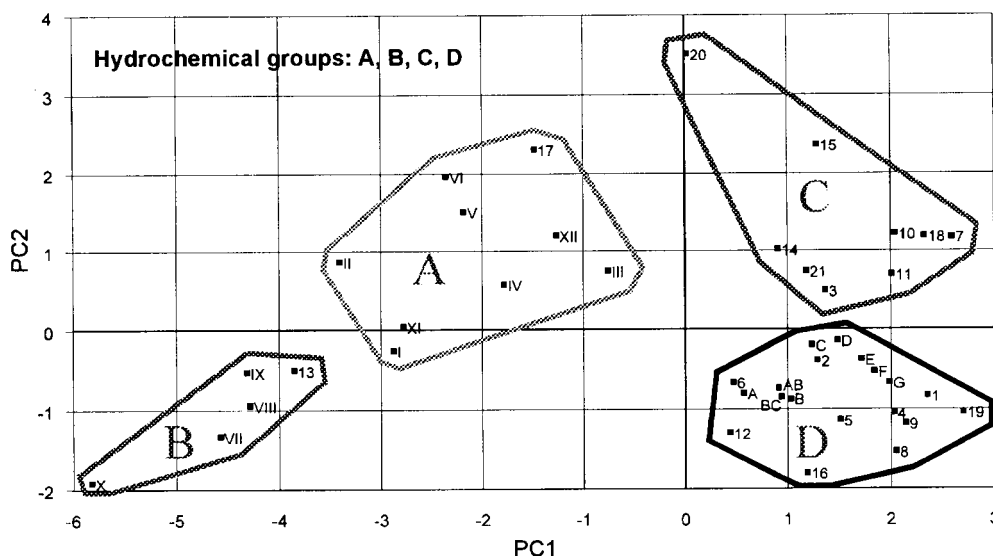


Figure 4. Ordering of water samples in relation to the first (PC1) and second (PC2) principal components for surface waters in the Kluda catchment

To distinguish characteristic spatial patterns of these physico-chemical water properties, Ward's method of hierarchical grouping was used (Ward, 1963; Hakamata *et al.*, 1992). The ionic macrocomposition was determined on the basis of standardized mean values (weighted means in the case of river water), as well as specific conductance figures. Using this method, it was possible to distinguish four hydrochemical groups (Table II). The distribution of water samples between groups is consistent with the results of principal components analysis presented above (Figure 4).

Hydrochemical groups A and B are characterized by the lowest concentrations of all the components under analysis (Table II). Their water is usually unsaturated and weakly acid, with an average pH of 6.7. Its other features are poor mineralization and low contents of calcium, magnesium, bicarbonate and ionized silica in proportion to sodium, chloride and sulphate ions. Using a Kolmogorov–Smirnov test at the  $\alpha = 0.05$  significance level, the goodness of fit between groups A and B was tested for each variable. It was found that statistically significant differences between groups A and B were defined by calcium, magnesium, chloride and sulphate ions, as well as specific conductance.

Such a chemical composition indicates that this is the type of water that passes quickly through the catchment, moving mainly through soil devoid of calcium carbonate, which has already been washed away or precipitated into lower soil horizons.

The spatial distribution of hydrochemical groups A and B coincides with the areas which permanently or seasonally lack any surface drainage. These groups include the water in ponds and intermittent streams

Table II. Mean values\* of physico-chemical properties of surface water within hydrochemical groups in the Kluda catchment

Parameter Groups	Ca	Mg	Na	K	HCO <sub>3</sub>	Cl	SO <sub>4</sub>	SiO <sub>2</sub>	s.e.c. ( $\mu\text{S cm}^{-1}$ )	pH
A	21.2	2.5	5.7	2.9	33.8	11.8	37.5	1.8	182	6.75
B	6.9	1.0	3.8	1.3	19.4	6.6	10.4	0.7	70	6.66
C	58.2	4.1	9.1	4.3	137.4	13.4	48.0	9.1	373	7.68
D	64.8	4.4	7.2	1.7	180.5	11.8	32.2	12.2	385	7.78

\* Units are  $\text{mg dm}^{-3}$  except for s.e.c. and pH



flowing out of ponds or wetlands. The chemical composition of water in these ponds is not homogeneous, as proved by their membership of two hydrochemical groups (A and B). In fact, concentrations of most of the components studied are twice as high in the water of locations in group A than in Group B. These differences can be interpreted as arising from lithological conditions, the nature of soil processes, and the degree to which ponds are overgrown by plants and/or filled by sediments. The low content of dissolved substances typical of the pond waters in group B indicates that a considerable proportion of the water is directly sourced from precipitation and that only a slight change in the water chemistry occurs during infiltration into the soil. This is largely a result of the undiversified lithology of the catchments containing those ponds, which features mainly permeable sand deposits with a low-capacity sorptive complex and no calcium carbonate. Their ionic contents, especially low in Lake Czarne, resemble the chemical composition of precipitation recorded at the rain gauging station at Storkowo (Figure 1) which has a mean specific conductance of  $37\mu\text{S cm}^{-1}$  (Mazurek, 1996).

The geological structure of the areas containing ponds from group A display a greater proportion of loams (weakly and heavy loamy sands lying on light loam) which affect the soil water regime and offer more possibilities for enriching the infiltrating rainwater with soluble components. Their increased salt contents may also be attributable to cultivation and the use of manure and fertilizers in most of the catchments around group A ponds, as well as continued overgrowing of small, shallow ponds (for example, ponds III and IV, in Figure 5).

Most of the samples of river water belong to hydrochemical groups C and D, with those in group D being more numerous. The water has a neutral pH, with the mean weighted pH index equal to 7.75. In comparison with the water of groups A and B, the water from localities included in groups C and D has higher specific conductance indices (ranging from  $259$  to  $437\mu\text{S cm}^{-1}$ ), significantly higher concentrations of calcium and bicarbonate ions and ionized silica, and slightly higher concentrations of magnesium and sodium cations. The localities associated with group C may be differentiated from those of group D on the basis of the concentrations of potassium and sulphate ions as well as the ionized silica contents.

As the proportion of groundwater supply in a stream flow increases, so does the proportion of solutes coming from the direct leaching of the substrate (carbonates and silica). The infiltrating rainwater has a greater opportunity (a longer time) to undergo a gradual chemical transformation within the soil profile and deeper substrate through processes such as adsorption, reduction, dissolution and cation exchange. However, groundwater is still aggressive towards calcium carbonate and calcite saturation indices (SI<sub>c</sub>) (White, 1988) range from  $-1.78$  to  $0.16$ . For both groups the chemical composition of stream water results primarily from the character of chemical weathering and, secondarily, from the contact time and flow paths of runoff reaching the river channel. Variation in the ionic concentration within the hydrochemical groups can also be attributed to the influence of seasonal fluctuations in biotic and weather conditions (such as air and soil temperature, evaporation, and soil moisture), because these factors modify the rate of soil leaching and migration of the particular ions. It should be emphasized that in this respect human activity has an insignificant impact on the catchment. This is due to extensive farming (mainly in the northeast and eastern parts of the catchment) and a low population density, which means that discharged quantities of municipal and household waste are significant only in the immediate vicinity of clustered settlements.

## SPATIAL PATTERNS OF SOLUTE TRANSPORT: WATER AND SOLUTE FLUXES IN DIFFERENT MORPHODYNAMIC ZONES

The significant variability in the physico-chemical parameters of surface water and their interrelations demonstrate how particular catchment areas make different contributions through the processes of soil and substrate leaching, and hence to the supply of dissolved material to the river channels. The geomorphological diversity of the Kluda catchment includes at least four morphodynamic zones, each with a distinctive runoff pathway and solute flux. These morphodynamic zones were designated as divide, plateau, escarpment and valley (Figure 5).

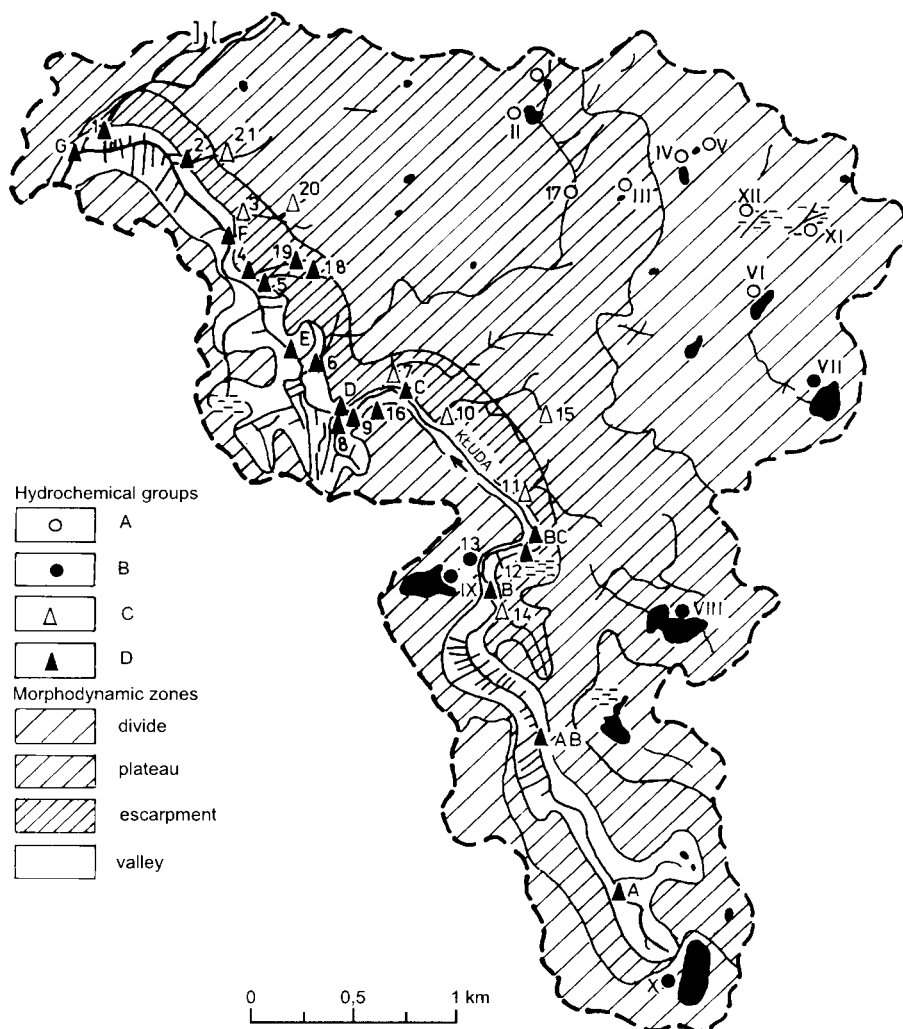


Figure 5. Spatial distribution of hydrochemical groups and morphodynamic zones derived by hydrological and hydrochemical mapping of the Kluda catchment

### *The divide morphodynamic zone*

This zone embraces the sub-catchments that lack outlets and those that only periodically drain to the main channel network (Figure 5). The mechanical composition of the brown soils occurring in the divide morphodynamic zone is favourable to a shallow sub-surface flow. However, the high lithological diversity of the zone indicates, that there are significant differences between the infiltration rates and water movement pathways in the sub-catchments of individual depressions.

Within this zone, there are eight water bodies in various stages of being overgrown by plants and filled with organic–mineral sediments, but most basins have open surface water only after snowmelt and heavier rains, and some of them occupy seasonal and perennial wetlands. A fragment of the divide zone has artificially acquired a seasonal connection to the perennial river network through drainage ditches or tile drain systems. During dry periods, however, these connections are severed owing to the lowering of the water table in the basins, and sub-catchments have no surface outlet. Under these conditions, the proportion of the Kluda

catchment without an outlet increases to almost 40 per cent, and the closed divide zone contributes to the outflow of water and matter only through the aquifer connected to the principal stream.

Surface water from the divide zone belongs to hydrochemical groups A and B. The aggressive nature of rain and snowmelt water and the acid pH index of the soil cover devoid of calcium carbonate determine the extent of leaching and, hence, the chemical properties of water in the closed basins. The concentration of ionic macrocomponents in surface waters is determined by their availability in the soil profile and susceptibility to the processes of ionic exchange and leaching, but is also modified by the water entering the biological cycle. On the basis of its chemical properties, surface water in this part of the catchment may be presumed to be derived either directly from precipitation and/or overland flow, or from discontinuous sub-surface water bodies.

#### *The plateau morphodynamic zone*

This zone is a slightly inclined plateau formed in weakly loamy sands and light loamy sands. The low terrain and permeable soils are responsible for the predominance of percolation and a longer residence time for water in the terrestrial part of the hydrologic cycle than occurs in the other zones. The zone is drained by second- and third-order streams fed by throughflow from local sub-surface water bodies and by groundwater from shallow-seated, water-bearing horizons with varying yields. The magnitude of the runoff supplied by groundwater is a function of, among other things, the depth of valley incision. Hence, groundwater provides an increasing proportion of runoff in streams in their lower reaches where they flow in deeply incised valleys that have developed near the plateau escarpments. Incised valleys have dissected the main groundwater water body and discharge from an individual unit may be perennial or intermittent, depending on its size and yield.

Spatial variability in the rate of leaching in the plateau zone results primarily from lithological and soil variability. The ionic composition and mineralization of water are the consequences of the aggressiveness of precipitation water and the acid pH index of soils devoid of  $\text{CaCO}_3$ . Infiltrating and percolating precipitation water undergoes a gradual chemical transformation in the soil profile. As the proportion of stream flow supplied by groundwater increases, so does the proportion of ions coming from the direct leaching of the substrate (carbonates and silica). The diversity of sources supplying streams in this zone is responsible for the different chemical compositions of its surface water and its inclusion in hydrochemical groups A, B and C (Figure 5).

At times of extreme weather conditions (for example during a drought or deep freezing of the ground), the leaching rate is a function not only of physico-chemical properties of deposits and the biochemical characteristics of the soil cover, but also of the total quantity of water in the terrestrial part of the hydrologic cycle and the depth of the water table. Climatic variability causes the supply of solutes from the plateau zone, via the river network to the basin outlet, to vary seasonally, and to increase with precipitation that generates high river flows and the 'wash out' of the substances accumulated in the soil profile. However, the overall contribution of the plateau zone tributaries to the dissolved load leaving the Kluda catchment is insubstantial (varying between an average of 1.1 per cent for site 2 and 3.3 per cent for site 6) and shows considerable differences over time, sporadically dropping even to zero (for example, sites 2, 3 and 6).

#### *The escarpment morphodynamic zone*

The escarpment zone lies between the plateau and the valley zones and is drained by first- and second-order streams fed by the natural outflows of groundwater draining the main aquifer. The topography of the Kluda basin dictates that these streams are short tributaries to the principal stream, with their sources far away from the main catchment boundary. Although the streams have small surface catchments, they are characterized by a fairly steady base flow throughout the year owing to the groundwater supply. Development of the river network in the plateau escarpment zone takes place through spring sapping of arcuate spring-head alcoves, thereby lengthening the valleys of the tributary and principal streams towards the plateau, and through the formation of new tributaries in the headwater areas. This system of development is consistent with Dunne's (1980) conceptual model for the development of a river network driven by the erosive action of groundwater (Schumm *et al.*, 1995). The volume of the dissolved load in river water is determined by the

abundance of the groundwater and the magnitude of leaching of the catchment sub-soil. The attributes that most river waters of this zone belong to hydrochemical group D, and that the dissolved load supplied to the Kluda by its streams is steady throughout the year, are the result of their being fed largely by groundwater. On average, the load constitutes from 4.5 per cent (site 4) to 7.7 per cent (site 5) of the total load exported from the Kluda basin.

#### *The valley morphodynamic zone*

The lowest morphodynamic zone in the catchment is the valley floor of the main stream, which represents the basal drainage level in the catchment. The valley floor is also the area where the groundwater table is shallowest. Saturation of areas along the Kluda River valley occurs not only because the water table is near the ground surface, but also because of the lithology, topography and the deep incision of the valley. Source areas adjacent to the mainstream generate saturation-excess overland flow during storm events and this is responsible for the rapid response of the river to precipitation. In this zone the movement of water and dissolved substances is primarily allochthonous in nature, being connected with the previously discussed zones.

An exception to this general condition concerns water moving through melt-out basins which play a special role in the movement of water in the valley zone. These basins collect shallow and deep groundwater flowing from the plateau. They are partly filled with mineral–organic deposits and are covered by meadow vegetation. The chemistry of water draining from the plateau via the melt-out basins is transformed as it is stored and slowly transmitted.

The results of hydrochemical mapping carried out along the course of the Kluda show that the chemistry of river water is similar to that of water in the wider catchment (measurement sites A–G, Figure 1). In the case of reaches flowing through multiple morpho-lithological units, the hydrochemical properties of the river water do not relate to the properties of the surrounding units in any clear-cut fashion. As a result, it may be concluded that river water chemistry is, in fact, controlled by supply routes and biochemical processes taking place in the channel. Flow paths and solute fluxes in the valley morphodynamic unit are, additionally, influenced by hydrochemical processes in the saturated sediments of the valley floor.

### CONCLUSION

The chemical characteristics of the surface water of the Kluda catchment vary spatially, and reflect the mosaic of postglacial lakeland environments. Hydrochemical mapping of the Kluda catchment has revealed relationships between its surface water chemistry and catchment relief, soils, lithology and the distribution of morphodynamic zones that are decisive in determining the soil water regime and the development of the river network. These factors control the nature, rate and distribution of denudation by geochemical processes and leaching, as well as the contact time of water and the supply of dissolved load to the river network.

Wide variations in the physico-chemical properties of surface waters and their interrelations demonstrate differences in the operation of soil and sub-soil leaching processes and, hence, the supply of dissolved material to ponds, lakes and rivers. The patchy nature of the source areas for both stream flow and the solutes that it contains ensures that the influence of leaching on the landscape is distributed non-uniformly.

The spatial distribution of morphogenic zones is an indicator of present tendencies in the relief development of postglacial areas. Most studies of water movement and leaching previously carried out in Poland have been performed in mountainous and upland areas with thin layers of skeletal soil and river discharges derived from overland flow, throughflow, or flow from shallow-seated aquifers. The results presented here represent conditions in postglacial environments, with highly variable geological structure, permeable deposits, thick soil profiles and high catchment retentiveness. These conditions fundamentally alter the pathways and the retention time of water moving through the catchment, shape the relationships between the discharge and solute concentrations (Mazurek, 1999), and control the intensity of denudation processes. The insights concerning the mechanics of water movement and the nature of the denudation processes gained in this study suggest that the relief of the postglacial zone is actually one of glacial and periglacial morphogenesis.

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